The Crystal Structure of Ezcurrite

Elio Cannillo, A. Dal Negro, and Luciano Ungaretti, Centro di Studio del C. N. R. per la Cristallografia strutturale, Istituto di Mineralogia dell’Università di Pavia, Italy

Abstract

The crystal structure of ezcurrite, a hydrous borate with chemical formula $2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$, has been solved by using direct methods. Three dimensional Weissenberg data (1974 reflections) gave a final $R$ factor of 0.050. The lattice parameters are: $a = 8.598$, $b = 9.570$, $c = 6.576 \, \text{Å}$, each $\pm 0.002$; $\alpha = 102^\circ 45'$, $\beta = 107^\circ 30'$, $\gamma = 71^\circ 31'$, each $\pm 3'$. Space group $P1$. The crystal structure of ezcurrite contains $[B_2O_6(OH)_2]^2-$ polyanions linked together to form chains along $c$. The polyanion is formed by two six-membered boron-oxygen rings, one consisting of two tetrahedra and one triangle, the other of two triangles and one tetrahedron. Therefore, the structural formula of ezcurrite is $[Na_2B_2O_6(OH)_2]:2H_2O$. The chains are linked together by the Na-polyhedra and by a network of hydrogen bonds.

Introduction

This investigation of the crystal structure of ezcurrite, $2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$, is part of a systematic study of hydrated borate minerals (Dal Negro et al., 1969, 1971). Ezcurrite was described as a new mineral by Muessig and Allen (1957) and restudied by Hurlbut and Aristarain in 1967. Christ (1960) proposed for ezcurrite a $[B_2O_6(OH)_2]^2-$ polyanion formed by two tetrahedra and three triangles. The occurrence and the chemical and physical properties of this mineral were fully described by Hurlbut and Aristarain; neither chemical analysis nor re-determination of the unit cell parameters were made on the sample used for this work.

Experimental

A colorless $0.11 \times 0.26 \times 0.64 \, \text{mm}$ fragment of ezcurrite from Tincalayu Mine, Salta, Argentina, elongated along [001] was studied. Relevant crystallographic data taken from Hurlbut and Aristarain (1967) are: $P1; a = 8.598$, $b = 9.570$, $c = 6.576 \, \text{Å}$ (each $\pm 0.002$); $\alpha = 102^\circ 45'$, $\beta = 107^\circ 30'$, $\gamma = 71^\circ 31'$ (each $\pm 3'$); $V = 484.7 \, \text{Å}^3$; cell content $Na_2[B_2O_6(OH)_2]:4H_2O$; specific gravity 2.049 (calc), 2.053 (meas).

Integrated Weissenberg photographs were taken using CuKα radiation and multiple film packs as the crystal was rotated about its $c$ axis. Lorentz-polarization and $\alpha-\alpha_2$ spot doubling corrections were applied to the photometrically measured intensities but no correction for absorption ($\mu = 25.5 \, \text{cm}^{-1}$) was made. Within the CuKα limiting sphere, 1974 independent reflections or about 90 percent of the 2198 present were collected. Of these, 893 were too weak to be accurately measured and were considered as unobserved.

Structure Analysis

The structure was solved by the use of direct methods. Sign determination was undertaken by applying the Sayre relationships to 374 reflections with normalized structure factors $|E| > 1.30$. The whole process was performed using a computer program written by R. E. Long (1965). On the $F_o$-map computed with the phases derived from the set with the highest consistency index, it was possible to find a number of maxima corresponding to the sodium and oxygen atoms. Successive three-dimensional Fourier syntheses, computed on the basis of these coordinates, gave the coordinates of all non-hydrogen atoms in the asymmetric unit. An $R$ factor of 0.19 was calculated from these coordinates. This reduced to 0.095 after three least-squares cycles carried out with the Busing, Martin and Levy (1962) computer program ORFLS, using the $f$-curves for neutral atoms of Na, O and B given by Hanson et al. (1964) and isotropic thermal parameters. At this stage isotropic convergence was attained and anisotropic thermal parameters were introduced. After two cycles the $R$ factor was reduced to 0.06.

A three-dimensional difference Fourier synthesis was computed, giving certain maxima which could be reasonably assigned to hydrogen atoms; however, the number of these peaks was greater than the number of hydrogens present in the unit cell, indicating that some peaks were spurious. Unfortunately it was possible to locate only five hydrogens out of seven because the difference map showed a smearing of the electron density around the two water molecules.

Another cycle of least-squares was undertaken using anisotropic thermal parameters for all non-hydrogen atoms; hydrogens were included in the
structure factor calculation with isotropic temperature factors equal to 3.0 for those belonging to the hydroxyls and 5.0 for the hydrogens belonging to the water molecules. This reduced the $R$ factor to 0.05 for the observed reflections. All the observed structure-factors were weighted equally during the refinement.

The final position parameters are listed in Table 1 and the observed and calculated structure factors are compared in Table 2.¹

**Description and Discussion of the Structure**

The main feature of the crystal structure of ezcurrite is the $[\text{B}_5\text{O}_7(\text{OH})_2]$⁻ unit first found in this structure (Fig. 1). These structural units are connected to form chains along $c$; two equivalent chains are present in a single unit cell (Fig. 2). The $[\text{B}_5\text{O}_7(\text{OH})_2]$⁻ group is formed by two six-membered boron–oxygen rings joined through a common tetrahedral boron. One of the rings consists of two triangles $\text{BO}_3$ and $\text{BO}_2(\text{OH})$ in addition to the cen-

¹To obtain a copy of Table 2, order NAPS Document 01978 from Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Check the most recent issue of this journal for the current address and prices.
According to the fourth rule of Christ (1960), the borate chain in ezcurrite may be considered as the first polymerization product of the still unknown isolated unit \([\text{B}_6\text{O}_{18}(OH)_6]^2-\), whereas the well-known \([\text{B}_3\text{O}_5(OH)]^2-\) sheets found in \(K_2[\text{B}_5\text{O}_8(OH)] \cdot 2\text{H}_2\text{O}\) (Marezio, 1969) in veatchite (Clark and Christ, 1971) and in gowerite (Konnert et al., 1972) represent the second step in the polymerization process.

The ezcurrite polyanion and the \([\text{B}_6\text{O}_{18}(OH)]^2-\) unit are similar, both being built of the same two six-membered rings. In ezcurrite, the mean planes of the two boron–oxygen rings are almost perpendicular, with an angle between the planes of 82.3°. Within the two six-membered rings, the internal B–B distances are nearly equal (2.472 Å is the mean value for the ring 1 and 2.473 Å for the ring 2). The first ring formed by O(7), O(8), O(10) is practically planar with a mean value for the internal angle of 119.5°, the greatest distance from the plane...
being -0.20 Å (Table 3). In comparison, the second ring built up by O(3), O(4), O(6) is less planar; the mean value for the internal angle is 117.4° and the greatest deviation from the plane is +0.95 Å. The polyanions link together to form chains with an angle B(5)–O(1)–B(1) of 127.5° and a separation B(5)–B(1) of 2.515 Å. The B–O distances in the ezcurrite polyanion (Table 4) are in good agreement with those found in the literature for other borates. The mean B–O bond length is 1.475 Å for the tetrahedral boron and 1.362 Å for triangular coordination. However, appreciable deviations from the average indicate that the B–O polyhedra are somewhat distorted. The O–B–O angles fall within the expected range (Table 4), as do the O–O distances (Table 5).

There are two independent sodium atoms in the ezcurrite structure (Fig.3), one being six-coordinated and the other seven. The sodium cations bond to the oxygen anions in two different centrosymmetrically related borate chains. Moreover, each Na–polyhedron shares an edge with another Na–polyhedron and the centrosymmetric pairs so formed link together through the vertex O(12) to form Na–O chains running along [111].

The two water molecules in the asymmetric unit are bonded only to the sodium atoms. In particular the water molecule O(11) is linked to Na(2) while O(12) connects the two independent Na–O polyhedra. The Na–O bond lengths range from 2.281 to 2.858 Å (Table 6). It has been possible to single out the hydrogens belonging to three hydroxyls (but

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**TABLE 6. Sodium coordinates in Ezcurrite.**

<table>
<thead>
<tr>
<th>Oxygen atom</th>
<th>Coordinates of oxygen atom</th>
<th>Na(1)–O distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>1.1755 0.2244 1.2169</td>
<td>2.436 (1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.6773 0.6135 1.0471</td>
<td>2.681 (1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>1.0798 0.1727 0.8132</td>
<td>2.438 (1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.9222 0.6072 1.1608</td>
<td>2.489 (1)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.9300 0.4115 0.6892</td>
<td>2.359 (1)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.8887 0.3299 1.4305</td>
<td>2.557 (1)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.8261 0.1440 0.9732</td>
<td>2.355 (1)</td>
</tr>
</tbody>
</table>

**Na(2)–O distance(Å)**

| O(2)        | 0.4110 0.0118 0.2130      | 2.676 (1)           |
| O(3)        | 0.5890 -0.0018 0.7850     | 2.373 (1)           |
| O(4)        | 0.4568 0.2564 0.2557      | 2.084 (1)           |
| O(5)        | 0.2845 0.2489 0.6009      | 2.533 (1)           |
| O(6)        | 0.8265 0.0547 0.4041      | 2.440 (1)           |
| O(7)        | 0.8261 0.1440 0.9732      | 2.355 (1)           |

Sodium atoms at E(2)-E in Table 1.
only one hydrogen for each water molecule). On the other hand there are only two O–O distances less than 3.1 Å involving the two water molecules, suggesting that two hydrogens do not form hydrogen bonds. Each B–O chain links to four other chains through the hydrogens belonging to the hydroxyl groups. The chain (Fig. 4) formed by the polyanion with atomic coordinates x, y, z of Table 1 is connected to two centrosymmetric chains through pairs of centrosymmetric hydrogen bonds. Two other chains, related by translations along a and c (atomic coordinates 1 + x, y, 1 + z and x – 1, y, z – 1), are linked to the first chain through one distinct hydrogen bond. In this way there is a thick network of hydrogen bonds which provides the connections among the polyanions and, through the water molecules, among polyanions and Na–polyhedra. The O–O distances involved in hydrogen-bonding and the O–H bond lengths are listed in Table 7.

Analysis of the anisotropic thermal parameters (Table 8) reveals that the thermal anisotropy of the atoms in euzcurrite is not large except for Na(2) and the water molecules. Taking into account the great anisotropy of Na(2) with respect to Na(1), the strong thermal motion of the O(12) water molecule can probably be explained as interaction between O(12) and Na(2), the major axis of the ellipsoid of thermal vibration for both atoms being localized along the bond direction.

Considering electrostatic balance, values ranging from 1.90 to 2.10 valence units are found for each oxygen atom on the basis of the correlations between bond length and bond strength given by Zachariasen (1963) for B–O and O–H . . . O bonds. Strengths of 1/7 = 0.142 and 1/6 = 0.166 valence units have been assigned to each oxygen atom coordinated to Na(1) and Na(2), respectively. One proton for each water molecule does not appear to form any hydrogen bonds, and for this reason a 1.0 valence was assigned to it.

### Acknowledgments

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### References


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